# Sediment-Water Column Exchange of Toxic Organic Compounds

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## **LONG-TERM GOAL**

Our long-term goals are to understand the mechanisms of contaminant exchange between the seabed and the overlying water column and the long-term, systemwide dispersal of contaminants in quiescent and energetic harbors.

## **OBJECTIVES**

The objectives of the study are

- 1. to test modeling predictions of water column concentrations of contaminants in quiescent environments;
- 2. to quantify the influence of sediment resuspension on net contaminant flux;
- 3. to quantify the rates and mechanisms of flushing within estuarine control volumes, and use those results to compare vertical and horizontal fluxes of different chemical constituents;
- 4. to apply a three-dimensional model to track particle-bound and dissolved contaminants in harbors during quiescent periods and extreme events;
- 5. to determine the influence of variations in forcing conditions (tides, river flow, and storms) on fluxes, net erosion and burial of contaminated sediments.

## **APPROACH**

The study focuses on two harbors, the relatively quiescent case of Inner Boston Harbor and the energetic Hudson River estuary. Control volumes are defined in each of the harbors, in which we evaluate the mass balances of organic pollutants (PAHs and PCBs) as dissolved, colloidal, and settling particle-bound species in the water column. Within these control volumes, we measure physical quantities required to make estimates of estuarine flushing rate, diffusive sublayer thickness, frequency and height of sediment resuspension, dispersion of suspended sediment, and particle size.

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Form Approved OMB No. 0704-0188 The control volume in the Hudson River is the estuarine turbidity maximum (ETM) region, adjacent to Manhattan Island. Measurements of physical variables and chemical concentrations are obtained north of, south of, and within the ETM. The Boston Harbor control volume is Boston Inner Harbor. Moorings and bottom tripods provide measurements of currents, salinity, temperature, and suspended sediment concentrations, as well as integrated measures of contaminants. Shipboard measurements include vertical profiles of chemical concentrations and water properties at selected time intervals. Sediment cores are also obtained throughout the estuary to determine sediment accumulation rates and reworking depths as well as to provide estimates of contaminant concentrations within the sediments.

Two levels of modeling will be accomplished, box modeling to constrain mass-balance estimates and determine the vertical and horizontal fluxes of contaminants, and three-dimensional modeling to obtain a process-level analysis of the mechanisms of vertical and horizontal exchange.

#### WORK COMPLETED

The first field study, focussing on the transport of contaminants in New York Harbor, has been completed. Most of the chemical analyses have been completed for this first field effort, and all of the physical data have been processed and subject to preliminary analysis. We are beginning to merge the physical and chemical data to determine the implications with respect to contaminant transport.

## **RESULTS**

The physical observations indicate intense resuspension within the turbidity maximum zone, with concentrations reaching 2000 mg/l during maximum spring tides. The intensity of resuspension decreases markedly to the north and south of the turbidity maximum, and it is also much lower during neap tides. The large difference in intensity of resuspension between neaps and springs indicates that there is a threshold for sediment resuspension of about 40 cm/s (near-bottom velocity), below which there is little resuspension.

The most notable aspect of the contaminant data was that the dissolved concentrations of PAHs were very low relative to the suspended fraction, even for the most water-soluble species. Dissolved concentrations were assessed using our new methodology in which polyethylene strips are allowed to equilibrate in the water column for periods of a day, and upon retrieval, these are extracted and analyzed for their PAH content. Such analyses reveal dissolved phenanthrene was typically 1-2 ng/l, compared to 50-100 ng/l for the total (dissolved + suspended) concentration. The ratio of dissolved-tototal concentration was similar for pyrene. Benzo(a)pyrene showed extremely low dissolved concentrations, as expected for a low-solubility compound. The large contribution of the suspended sediment to the total PAH concentration is due in part to the high concentrations of suspended sediment (averaging 350 mg/l during spring tides at the turbidity maximum zone). However the estimated distribution coefficients are much higher than those derived from the octanol-water partition coefficient and the estimated organic content of the suspended sediment. This may be explained by high concentrations of soot in the sediment, which effectively binds even the low molecular weight PAHs and may explain the low apparent release of PAHs to the water column. The sediments in the turbidity maximum zone appear to be an important source of contaminants to the water column, based on the spatial distributions of PAHs as well as the dominance of the suspended fraction in the total PAH distribution.

Another important finding in this study is the seasonal reworking of bottom sediments, which may greatly increase the reservoir of contaminants that is exposed to the water column relative to tidal resuspension. A maximum of 0.5–1 cm of sediment may be resuspended during an individual tidal cycle, but our sediment cores indicate that physical reworking may occur to depths of 10-20 cm due to the seasonal variations in the estuarine circulation regime. During high flow in the spring, the salinity front is pushed toward the mouth of the estuary, causing erosion of sediment at the turbidity maximum zone and deposition close to the mouth. When the river flow decreases, the salinity front returns to its normal position, and sediment moves back from the temporary deposit at the mouth to the turbidity maximum. This seasonal redistribution of sediment causes the re-exposure of a large mass of contaminants that had been buried during the previous year. This process may greatly increase the exposure time of contaminants within estuaries.

## **IMPACT/APPLICATION**

This research has important potential implications in quantifying the release of contaminants from sediments in a wide range of environmental conditions. The results will have an important bearing on remediation strategies, modeling of contaminant transport, and risk assessment.

## **TRANSITIONS**

The preliminary results of this study are just beginning to be communicated, so there has not yet been impact in other research or applications.

## RELATED PROJECTS

Geyer is receiving support from the Hudson River Foundation to study the sediment transport and trapping processes in the Hudson River estuary. Geyer is also receiving ONR support for studies of sediment transport by river plumes during floods. Gschwend is receiving support from NSF to try to isolate soot from coastal sediments and assess this medium as a sorbent for PAHs and PCBs. Gschwend is also receiving support from Sea Grant to evaluate the hypothesis that benthic infauna do not bioaccumulate PAHs due to the effective "sequestration" of these compounds when they are bound up in soot.